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EXHAUST EMISSION CONTROL SYSTEM FOR INTERNAL COMBUSTION ENGINE.

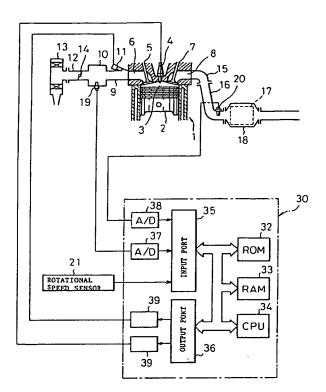
(iv) An NOx absorbing agent (17) is disposed inside an exhaust gas passage of a combustion engine. This NOx absorbing agent (17) absorbs NOx when the air/fuel ratio of exhaust gas flowing thereinto is lean, and discharges NOx which it has absorbed when the air/fuel ratio of exhaust gas flowing

thereinto becomes rich. When the air/fuel ratio of exhaust gas flowing into the NOx absorbing agent (17) is to be made rich so as to discharge NOx from the NOx absorbing agent, a higher NOx absorbing agent temperature makes the degree of richness higher and rich time shorter.

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Fig.1



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TECHNICAL FIELD

The present invention relates to an exhaust purification device of an internal combustion engine.

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BACKGROUND ART

A diesel engine in which an engine exhaust passage is branched to a pair of exhaust branch passages for purifying NOx in the diesel engine, a switching valve is disposed at the branched portion of these exhaust branch passages, the switching valve is switched each time a predetermined time passes to alternately guide the exhaust gas to one of the exhaust branch passages, and a catalyst which can oxidize and absorb the NOx is disposed in each of the exhaust branch passages is well known (refer to Japanese Unexamined Patent Publication No. 62-106826). In this diesel engine, the NOx in the exhaust gas introduced into one exhaust branch passage is oxidized and absorbed by the catalyst disposed in that exhaust branch passage. During this time, the inflow of the exhaust gas to the other exhaust branch passage is stopped and, at the same time, a gaseous reducing agent is fed into this exhaust branch passage. The NOx accumulated in the catalyst disposed in this exhaust branch passage is reduced by this reducing agent. Subsequently, after the elapse of a predetermined time, the introduction of the exhaust gas to the exhaust branch passage to which the exhaust gas had been introduced heretofore is stopped by the switching function of the switching valve, and the introduction of the exhaust gas to the exhaust branch passage to which the introduction of the exhaust gas had been stopped heretofore is started again. That is, in this diesel engine, seen from the viewpoint of each of the exhaust branch passages, exhaust gas is made to flow for a predetermined time during which the NOx in the exhaust gas is oxidized and absorbed by the catalyst, then the inflow of exhaust gas is stopped for a predetermined period and a reducing agent is fed, whereby the NO_x accumulated in the catalyst is reduced.

However, in this diesel engine, when the NO_x was to be reduced, there was the problem that the inflow of the exhaust gas to the catalyst was stopped, but that the NO_x was attempted to be reduced while causing exhaust gas to flow into the catalyst. That is, with such a catalyst, the speed of reduction of the NO_x changed depending on the temperature of the catalyst and as the temperature of the catalyst became lower, the speed of reduction of the NO_x became slower. Accordingly, where the temperature of the catalyst is low, if a reducing agent is fed for a predetermined period, when the period of feeding the reducing agent is short, the NO_x

absorbed in the catalyst cannot be sufficiently reduced, so a large amount of NO_x remains in the catalyst and therefore the NO_x absorptioncapacity ends up being reduced. As a result, there was the problem that the NO_x absorption capacity becomes saturated in a short time after the feeding of the reducing agent is stopped and the NO_x absorption action started and therefore the NO_x is released into the atmosphere.

Further, if a large amount of the reducing agent is fed when the temperature of the catalyst is low, only a small amount of the reducing agent is used for the reduction of the NOx due to the slow speed of reduction of the NOx, therefore there was the problem that a large amount of the reducing agent is released in the atmosphere. On the other hand, if the amount of the reducing agent is reduced to solve this problem, then even when the temperature of the catalyst is high and therefore the speed of reduction of NO_x is fast, only part of the NO_x is reduced and therefore a large amount of NOx remains in the catalyst, so the NOx absorption capacity ends up reduced. As a result, there is the problem that the NOx absorption capacity ends up saturated in a short time after the feeding of the reducing agent is stopped and the NOx absorption action is started and therefore the NOx is released into the atmosphere.

DISCLOSURE OF THE INVENTION

An object of the present invention is to provide an exhaust purification device which suppresses the release of harmful components into the atmosphere at the time of reducing NO_x .

According to the present invention, there is provided an exhaust purification device of an internal combustion engine which has in an engine exhaust passage a NOx absorbent which absorbs the NOx when the air-fuel ratio of the inflowing exhaust gas is lean and which releases the absorbed NOx when the air-fuel ratio of the inflowing exhaust gas becomes rich and which is provided with a temperature detecting means for detecting a temperature representing the temperature of the NO_x absorbent and a NO_x release controlling means for making the air-fuel ratio of the exhaust gas flowing into the NOx absorbent rich when the NOx is to be released from the NOx absorbent and at that time increasing the degree of richness or shortening the time the ratio is made rich the higher the temperature representing the temperature of the NO_x absorbent.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is an overall view of an internal combustion engine; Fig. 2 is a diagram showing a map

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of a basic fuel injection time; Fig. 3 is a diagram showing a correction coefficient K; Fig. 4 is a graph schematically showing the concentration of unburnt HC, CO, and oxygen in the exhaust gas discharged from the engine; Fig. 5 is a diagram for explaining an absorption and release function of the NOx; Fig. 6 is a diagram showing the amount of NOx discharged from the engine, Fig. 7 is a graph showing the capacity of absorption of NOx of the NOx absorbent; Fig. 8 is a graph showing the characteristics of release of NOx; Fig. 9 is a graph showing the change in the correction coefficient K; Fig. 10 is a graph showing C_1 , C_2 , α , and β ; Fig. 11 is a diagram showing a map of the exhaust gas temperature T; Fig. 12 and Fig. 13 are flow charts showing a time interruption routine; Fig. 14 is a flow chart for calculating the fuel injection time TAU; and Fig. 15 is an overall view of an internal combustion engine showing another embodiment.

BEST MODE FOR CARRYING OUT THE INVENTION

Figure 1 shows a case where the present invention is applied to a gasoline engine.

Referring to Fig. 1, 1 denotes an engine body; 2, a piston; 3, a combustion chamber; 4, a spark plug; 5, an intake valve; 6, an intake port; 7, an exhaust valve; and 8, an exhaust port, respectively. The intake port 6 is connected to a surge tank 10 via a corresponding branch pipe 9, and a fuel injector 11 injecting the fuel toward the interior of the intake port 6 is attached to each branch pipe 9. The surge tank 10 is connected to an air cleaner 13 via an intake duct 12, and a throttle valve 14 is disposed in the intake duct 12. On the other hand, the exhaust port 8 is connected via an exhaust manifold 15 and an exhaust pipe 16 to a casing 18 including a NO_x absorbent 17.

An electronic control unit 30 comprises a digital computer and is provided with a ROM (read only memory) 32, a RAM (random access memory) 33, a CPU (microprocessor) 34, an input port 35, and an output port 36, which are interconnected by a bidirectional bus 31. In the surge tank 10 is mounted a pressure sensor 19 for generating an output voltage proportional to the absolute pressure in the surge tank 10. The output voltage of this pressure sensor 19 is input through an AD converter 37 to the input port 35. Further, a temperature sensor 20 which generates an output voltage proportional to the temperature of the exhaust gas is attached in the exhaust pipe 16 upstream of the casing 18. The output voltage of this temperature sensor 20 is input through an AD converter 38 to the input port 35. Further, the input port 35 is connected to it a rotational speed sensor 21 for generating an output pulse expressing the engine

rotational speed. On the other hand, the output port 36 is connected through a corresponding drive circuit 39 to a spark plug 4 and fuel injector 11.

In the internal combustion engine shown in Fig. 1, the fuel injection time TAU is calculated based on for example the following equation.

TAU = TP.K

where, TP is a basic fuel injection time, and K is a correction coefficient. The basic fuel injection time TP shows the fuel injection time necessary for bringing the air-fuel ratio of an air-fuel mixture fed into the engine cylinder to the stoichiometric airfuel ratio. This basic fuel injection time TP is found in advance by experiments and is stored in advance in the ROM 32 in the form of a map as shown in Fig. 2 as the function of the absolute pressure PM in the surge tank 10 and the engine rotational speed N. The correction coefficient K is a coefficient for controlling the air-fuel ratio of the airfuel mixture fed into the engine cylinder, and if K = 1.0, the air-fuel mixture fed into the engine cylinder becomes the stoichiometric air-fuel ratio. Contrary to this, when K becomes smaller than 1.0, the air-fuel ratio of the air-fuel mixture fed into the engine cylinder becomes larger than stoichiometric air-fuel ratio, that is, becomes lean, and when K becomes larger than 1.0, the air-fuel ratio of the air-fuel mixture fed into the engine cylinder becomes smaller than the stoichiometric air-fuel ratio, that is, becomes rich.

The value of this correction coefficient K is predetermined in relation to the absolute pressure PM in the surge tank 10 and the engine rotational speed N. Figure 3 shows an embodiment of the value of the correction coefficient K. In the embodiment shown in Fig. 3, in the region where the absolute pressure PM in the surge tank 10 is relatively low, that is, in the engine low and medium load operation region, the value of the correction coefficient K is made a value smaller than 1.0, therefore at this time the air-fuel ratio of the air-fuel mixture fed into the engine cylinder is made lean. On the other hand, in the region where the absolute pressure PM in the surge tank 10 is relatively high, that is, in the engine high load operation region, the value of the correction coefficient is made 1.0. Accordingly, at this time, the air-fuel ratio of the airfuel mixture fed into the engine cylinder is made the stoichiometric air-fuel ratio. Further, in the region where the absolute pressure PM in the surge tank 10 becomes the highest, that is, in the engine full load operation region, the value of the correction coefficient is made a value larger than 1.0. Therefore, at this time, the air-fuel ratio of the airfuel mixture fed into the engine cylinder is made rich. An internal combustion engine is usually op-

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erated most frequently with a low and medium load and therefore for the majority of the period of operation a lean air-fuel mixture is burned.

Figure 4 schematically shows the concentration of representative components in the exhaust gas discharged from the combustion chamber 3. As seen from Fig. 4, the concentration of the unburnt HC and CO in the exhaust gas discharged from the combustion chamber 3 is increased as the air-fuel ratio of the air-fuel mixture fed into the combustion chamber 3 becomes richer, and the concentration of the oxygen O_2 in the exhaust gas discharged from the combustion chamber 3 is increased as the air-fuel ratio of the air-fuel mixture fed into the combustion chamber 3 becomes leaner.

The NO_x absorbent 17 contained in the casing 18 uses, for example, alumina as a carrier. On this carrier, at least one substance selected from alkali metals, for example, potassium K, sodium Na, lithium Li, and cesium Cs; alkali earths, for example, barium Ba and calcium Ca; and rare earths, for example, lanthanum La and yttrium Y and a precious metal such as platinum Pt are carried. When referring to the ratio between the air and fuel (hydrocarbons) fed into the intake passage of the engine and the exhaust passage upstream of the NO_x absorbent 17 as the air-fuel ratio of the inflowing exhaust gas flowing into the NOx absorbent 17, this NO_x absorbent 17 performs the absorption and releasing function of NOx byabsorbing the NOx when the air-fuel ratio of the inflowing exhaust gas is lean, while releasing the absorbed NOx when the concentration of oxygen in the inflowing exhaust gas falls. Note that, where the fuel (hydrocarbons) or air is not fed into the exhaust passage upstream of the NOx absorbent 17, the air-fuel ratio of the inflowing exhaust gas coincides with the air-fuel ratio of the air-fuel mixture fed into the combustion chamber 3, and accordingly in this case, the NOx absorbent 17 absorbs the NOx when the air-fuel ratio of the air-fuel mixture fed into the combustion chamber 3 is lean and releases the absorbed NOx when the concentration of oxygen in the air-fuel mixture fed into the combustion chamber 3 is lowered.

When the above-mentioned NO_x absorbent 17 is disposed in the exhaust passage of the engine, this NO_x absorbent 17 actually performs the absorption and releasing function of NO_x, but there are areas of the exact mechanism of this absorption and releasing function which are not clear. However, it can be considered that this absorption and releasing function is conducted by the mechanism as shown in Fig. 5. This mechanism will be explained by using as an example a case where platinum Pt and barium Ba are carried on the carrier, but a similar mechanism is obtained even if another precious metal, alkali metal, alkali earth, or

rare earth is used.

Namely, when the inflowing exhaust gas becomes considerably lean, the concentration of oxygen in the inflowing exhaust gas is greatly increased. As shown in Fig. 5(A), the oxygen O_2 is deposited on the surface of the platinum Pt in the form of O_2^- or O^2^- . On the other hand, the NO in the inflowing exhaust gas reacts with the O_2^- or O^2^- on the surface of the platinum Pt and becomes NO_2 (2NO + O_2 \rightarrow 2NO₂). Subsequently, a part of the produced NO_2 is oxidized on the platinum Pt and absorbed into the absorbent. While bonding with the barium oxide BaO, it is diffused in the absorbent in the form of nitric acid ions NO_3^- as shown in Fig. 5(A). In this way, NO_x is absorbed into the NO_x absorbent 17.

So long as the oxygen concentration in the inflowing exhaust gas is high, the NO2 is produced on the surface of the platinum Pt, and so long as the NO_x absorption ability of the absorbent is not saturated, the NO2 is absorbed into the absorbent and nitric acid ions NO₃ are produced. Contrary to this, when the oxygen concentration in the inflowing exhaust gas is lowered and the production of NO2 is lowered, the reaction proceeds in an inverse direction (NO₃⁻ → NO₂), and thus nitric acid ions NO₃ in the absorbent are released in the form of NO2 from the absorbent. Namely, when the oxygen concentration in the inflowing exhaust gas is lowered, the NOx is released from the NOx absorbent 17. As shown in Fig. 4, when the degree of leanness of the inflowing exhaust gas becomes low, the oxygen concentration in the inflowing exhaust gas is lowered, and accordingly when the degree of leanness of the inflowing exhaust gas is lowered, the NOx is released from the NOx absorbent 17 even if the air-fuel ratio of the inflowing exhaust gas is lean.

On the other hand, at this time, when the airfuel ratio of the air-fuel mixture fed into the combustion chamber 3 is made rich and the air-fuel ratio of the inflowing exhaust gas becomes rich, as shown in Fig. 4, a large amount of unburnt HC and CO is discharged from the engine, and these unburnt HC and CO react with the oxygen O2 or O2- on the platinum Pt and are oxidized. Also, when the air-fuel ratio of the inflowing exhaust gas becomes rich, the oxygen concentration in the inflowing exhaust gas is extremely lowered, and therefore the NO2 is discharged from the absorbent. This NO2 reacts with the unburnt HC and CO as shown in Fig. 5(B) and is reduced. In this way, when the NO2 no longer exists on the surface of the platinum Pt, the NO2 is successively released from the absorbent. Accordingly, when the air-fuel ratio of the inflowing exhaust gas is made rich, the NO_x is released from the NO_x absorbent 19 in a short time.

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Namely, when the air-fuel ratio of the inflowing exhaust gas is made rich, first of all, the unburnt HC and CO immediately react with the O2 or O2on the platinum Pt and are oxidized, and subsequently if the unburnt HC and CO still remain even though the O₂ or O² on the platinum Pt is consumed, the NOx released from the absorbent and the NOx discharged from the engine are reduced by these unburnt HC and CO. Accordingly, when the air-fuel ratio of the inflowing exhaust gas is made rich, the NOx absorbed in the NOx absorbont 17 is released in a short time and in addition this released NOx is reduced, and therefore the discharge of NOx into the atmosphere can be blocked. Also, since the NOx absorbent 17 has the function of a reduction catalyst, even if the air-fuel ratio of the inflowing exhaust gas is made the stoichiometric air-fuel ratio, the NOx released from the NO_x absorbent 17 can be reduced. However, where the air-fuel ratio of the inflowing exhaust gas is made the stoichiometric air-fuel ratio, the NOx is released merely gradually from the NOx absorbent 17, and therefore a slightly long time is required for releasing all NO_x absorbed in the NO_x absorbent

When the degree of leanness of the inflowing exhaust gas is lowered as mentioned before, even if the air-fuel ratio of the inflowing exhaust gas is lean, the NOx is released from the NOx absorbent 17. Accordingly, so as to release the NOx from the NO_x absorbent 17, it is satisfactory if the concentration of oxygen in the inflowing exhaust gas is lowered. Note, even if the NOx is released from the NO_x absorbent 17, when the air-fuel ratio of the inflowing exhaust gas is lean, the NOx is not reduced in the NO_x absorbent 17, and accordingly, in this case, it is necessary to provide a catalyst which can reduce the NOx downstream of the NOx absorbent 17 or supply a reducing agent downstream of the NOx absorbent 17. Of course, it is also possible to reduce the NOx downstream of the NO_x absorbent 17 in this way, but it is rather preferable that the NOx be reduced in the NOx absorbent 17. Accordingly, in the embodiment according to the present invention, when the NOx should be released from the NO_x absorbent 17, the air-fuel ratio of the inflowing exhaust gas is made rich, whereby the NOx released from the NOx absorbent 17 is reduced in the NO_x absorbent 17.

However, in the embodiment according to the present invention, as mentioned above, during full load operation, the air-fuel mixture fed into the engine cylinder 3 is made rich and during high load operation, the air-fuel mixture is made the stoichiometric air-fuel ratio, so during the full load operation and the high load operation, the NO_x is released from the NO_x absorbent 17. However, if the frequency of this full load operation or high

load operation is small, then even if the NO_x is released from the NO_x absorbent 17 only during full load operation and high load operation, the absorption capacity of the NO_x by the NO_x absorbent 17 will end up becoming saturated during the time when a lean air-fuel mixture is burnt and therefore it will end up becoming impossible for the NO_x absorbent 17 to absorb the NO_x . Accordingly, in the embodiment according to the present invention, when a lean air-fuel mixture continues to be burnt, the air-fuel mixture fed into the combustion chamber 3 is cyclically made rich and during this time the NO_x is released from the NO_x absorbent 17.

In this case, however, if the cycle at which the air-fuel mixture fed into the engine cylinder 3 is made rich is long, then the NOx absorbing capacity of the NO_x absorbent 17 will end up becoming saturated during the time the lean air-fuel mixture is being burnt and therefore the NOx can no longer be absorbed in the NOx absorbent 17, so there will be the problem that NOx will end up being released into the atmosphere. As opposed to this, even if an engine operating state where a large amount of NO_x is discharged from the engine continues, if the cycle at which the air-fuel mixture is made lean is shortened so that the NOx is released from the NOx absorbent 17 before the NOx absorbing capacity of the NO_x absorbent 17 becomes saturated, then this time the problem will arise of an increase of the amount of fuel consumption.

Therefore, in the present invention, the amount of NO_x which is absorbed in the NO_x absorbent 17 is found and the air-fuel mixture is made rich when the amount of the NO_x absorbed in the NO_x absorbent 17 exceeds a predetermined allowable value. If the air-fuel mixture is made rich when the amount of the NO_x absorbed in the NO_x absorbent 17 exceeds a predetermined allowable value, then the NO_x absorbing capacity of the NO_x absorbent 17 will never become saturated, so the NO_x will no longer be released into the atmosphere and, further, the frequency at which the air-fuel mixture is made rich can be reduced as well, so it is possible to suppress an increase in the amount of the fuel consumption.

However, when finding the amount of NO_x being absorbed in the NO_x absorbent 17, it is difficult to directly find the amount of NO_x being absorbed in the NO_x absorbent 17. Therefore, in the embodiment according to the present invention, the amount of the NO_x absorbed in the NO_x absorbent 17 is estimated from the amount of NO_x in the exhaust gas discharged from the engine. That is, the higher the rotational speed N of the engine, the larger the amount of exhaust gas discharged per unit time from the engine, so as the engine rotational speed N becomes higher, the amount of NO_x

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discharged from the engine per unit time increases. Further, the higher the engine load, that is, the higher the absolute pressure PM in the surge tank 10, the greater the amount of the exhaust gas discharged from the combustion chambers 3 and further the higher the combustion temperature, so the higher the engine load, that is, the higher the absolute pressure PM in the surge tank 10, the greater the amount of NO_x discharged from the engine per unit time.

Figure 6(A) shows the relationship between the amount of the NO_x discharged from the engine per unit time, the absolute pressure PM in the surge tank 10, and the engine rotational speed N as found by experiments. In Fig. 6(A), the curves show the identical amounts of NO_x . As shown in Fig. 6(A), the amount of NO_x discharged from the engine per unit time becomes larger the higher the absolute pressure PM in the surge tank 10 and becomes larger the higher the engine rotational speed N. Note that the amount of NO_x shown in Fig. 6(A) is stored in the ROM 32 in advance in the form of a map as shown in Fig. 6(B).

On the other hand, Fig. 7 shows the relationship between the absorption capacity NO_xCAP which can be absorbed by the NO_x absorbent 17 and the temperature T of the exhaust gas, which represents the temperature of the NOx absorbent 17. If the temperature of the NO_x absorbent 17 becomes lower, that is, the temperature T of the exhaust gas becomes lower, the oxidation action of the NO_x (2NO + $O_2 \rightarrow 2NO_2$) is weakened, and therefore the NO_x absorption capacity NO_xCAP is lowered. Further, if the temperature of the NO_x absorbent 17 becomes higher, that is, the temperature T of the exhaust gas becomes higher, the NO_x absorbed in the NO_x absorbent 17 is decomposed and naturally released, so the NOx absorption capacity NO_xCAP is lowered. Accordingly, the NO_x absorption capacity NOxCAP becomes larger between about 300 °C to about 500 °C.

On the other hand, Fig. 8 shows the results of experiments on the amount of NOx released from the NO_x absorbent 17 when switching the air-fuel ratio of the exhaust gas flowing into the NOx absorbent 17 from lean to rich. Note that the solid line in Fig. 8 shows the state when the temperature of the NO_x absorbent 17, that is, the temperature T of the exhaust gas, is high, while the broken line shows when the temperature of the NOx absorbent 17, that is, the temperature T of the exhaust gas, is low. The rate of decomposition of the NO_x in the NO_x absorbent 17 becomes faster the higher the temperature of the NOx absorbent 17. Therefore, when the temperature of the NOx absorbent 17 is high, as shown by the solid line in Fig. 8, that is, when the temperature T of the exhaust gas is high, a large amount of NOx is released from the NOx

absorbent 17 in a short time, while when the temperature of the NO_x absorbent 17, that is, the temperature T of the exhaust gas, is low, as shown by the broken line in Fig. 8, a small amount of NO_x is continually released from the NO_x absorbent 17 over a long period. That is, the higher the temperature T of the exhaust gas, the greater the amount of NO_x released from the NO_x absorbent 17 per unit time and the shorter the release time of the NO_x .

When the amount of the unburnt HC and CO discharged from the engine, however, is smaller than the amount which can reduce the total NOx released from the NO_x absorbent 17, part of the NO_x is released into the atmosphere without being reduced, while when the amount of unburnt HC and CO discharged from the engine is greater than the amount able to reduce the total NOx released from the NO_x absorbent 17, the excess unburnt HC and CO are released into the atmosphere. Accordingly, to prevent the NOx and the unburnt HC and CO from being released into the atmosphere, it is necessary to discharge exactly the amount of the unburnt HC and CO from the engine needed to reduce the NOx released from the NOx absorbent 17. Toward this end, it becomes necessary to increase the amount of the unburnt HC and CO in accordance with the curve shown in Fig. 8.

As mentioned earlier, however, the amount of the unburnt HC and CO discharged from the engine is proportional to the degree of richness of the air-fuel mixture fed into the combustion chamber 3. Therefore, in the present invention, as shown in Fig. 9, the value of the correction coefficient k with respect to the basic fuel injection time TP, that is, the degree of richness of the air-fuel mixture, is made to change in accordance with a pattern as close as possible to the pattern of change of the concentration of NOx shown in Fig. 8. Note that here, the correction coefficient k has the relationship K = 1 + k with the above-mentioned correction coefficient K and therefore when k = 0, the air-fuel mixture becomes the stoichiometric air-fuel ratio while when k > 0, the air-fuel mixture becomes rich. Therefore, it is understood from Fig. 9 that the higher the temperature of the NO_x absorbent 17, the higher the degree of richness and the shorter the time the ratio is made rich.

As shown by the solid line in Fig. 9, when the NO_x is to be released from the NO_x absorbent 17, the correction coefficient k is made to rise by α increments with each passing of the unit time until the time C reaches C_1 . Next, when the time C is between C_1 and C_2 , the correction coefficient k is held constant, then when the time C exceeds C_2 , the correction coefficient k is made to descend in β decrements with each unit time. The values of these α , β , C_1 , and C_2 are set so that the pattern of

change of the correction coefficient k becomes as close as possible to the pattern of change of the concentration of NO_x shown by the solid line in Fig. 8.

On the other hand, the pattern of change of the correction coefficient k when the temperature of the NO_x absorbent 17, that is, the temperature T of the exhaust gas, is low, is also set so that it becomes as close as possible to the pattern of change of the concentration of NOx when the temperature T of the exhaust gas is low, as shown by the broken line in Fig. 8. In this case, to make the pattern of change of the correction coefficient k in Fig. 9 like the broken line, it is understood that it is sufficient to make both α and β smaller and make C_1 and C_2 larger. That is, to make the pattern of change of the correction coefficient k close to the pattern of change of the concentration of NO_x shown in Fig. 8, it is sufficient to make α and β larger and make C₁ and C₂ smaller as the temperature T of the exhaust gas becomes higher, as shown in Fig. 10. Note that the relationship between C_1 , C_2 , α , and β and the temperature T of the exhaust gas shown in Fig. 10 is stored in advance in the ROM 32.

Note that in the embodiment according to the present invention, provision is made of a temperature sensor 25 for detecting the temperature T of the exhaust gas and accordingly the NOx absorption capacity NO_x CAP shown in Fig. 7 and the α , β, C₁, and C₂ shown in Fig. 10 are determined based on the temperature T of the exhaust gas detected by this temperature sensor 25. The temperature T of the exhaust gas, however, can be estimated from the absolute pressure PM in the surge tank 10 and the engine rotational speed N. Therefore, instead of providing the temperature sensor 25, it is possible to store the temperature T of the exhaust gas in the ROM 32 in advance in the form of a map as shown in Fig. 11 and determine the NO_x absorption capacity NO_x CAP and α , β , C₁, and C₂ based on the temperature T of the exhaust gas obtained from this map.

Next, an explanation will be made of the first embodiment of control of the release of NO_x with reference to Fig. 12 to Fig. 14.

Figure 12 and Fig. 13 show a time interruption routine executed by interruption every predetermined time.

Referring to Fig. 12 and Fig. 13, first, at step 100, it is judged if a NO_x release flag showing that the NO_x should be released from the NO_x absorbent 17 is set or not. When the NO_x release flag is not set, the routine proceeds to step 101, where it is judged if the correction coefficient K is smaller than 1.0, that is, if the operating state is one in which the air-fuel mixture should be made lean. When K < 1.0, that is, when the operating state is one in which the air-fuel mixture should be made

lean, the routine proceeds to step 102, where the count D is made zero, then the routine proceeds to step 103.

At step 103, the NO_x amount Nij discharged from the engine per unit time is calculated from the map shown in Fig. 6(B) based on the absolute pressure PM in the surge tank 10, detected by the pressure sensor 19, and the engine rotational speed N. Next, at step 104, the NO_x amount Nij is multiplied by the interruption time interval Δt and the product Nij* ΔT is added to ΣNO_x . The product Nij* Δt shows the amount of the NO_x discharged from the engine during the interruption time interval Δt . At this time, the NO_x discharged from the engine is absorbed by the NO_x absorbent 17, so ΣNO_x shows the estimated value of the amount of NO_x absorbed in the NO_x absorbent 17.

Next, at step 105, the NO $_{\rm x}$ absorption capacity NO $_{\rm x}$ CAP is calculated from the relationship shown in Fig. 7 based on the temperature T of the exhaust gas detected by the temperature sensor 25. Next, at step 106, it is judged if the estimated value Σ NO $_{\rm x}$ of the amount of NO $_{\rm x}$ absorbed in the NO $_{\rm x}$ absorbent 17 has exceeded the NO $_{\rm x}$ absorption capacity NO $_{\rm x}$ CAP When Σ NO $_{\rm x}$ \leq NO $_{\rm x}$ CAP, the processing cycle is completed. At this time, a lean airfuel mixture is burned and the NO $_{\rm x}$ discharged from the engine is absorbed in the NO $_{\rm x}$ absorbent 17.

On the other hand, if it is judged at step 106 that $\Sigma NO_x > NO_x CAP$, that is, the NO_x absorption capacity of the NOx absorbent 17 is saturated, the routine proceeds to step 107, where the NOx release flag is set. Next, at step 108, C_1 , C_2 , α , and B are calculated from the relation shown in Fig. 10 based on the temperature T of the exhaust gas and the processing cycle is ended. If the NOx release flag is set, at the next processing cycle, the routine proceeds from step 100 to step 109, where the count C is incremented by one. Next, at step 110, it is judged if the count C is smaller than C1. When $C < C_1$, the routine proceeds to step 111, where α is added to the correction coefficient k. Next, the processing cycle is ended. The action of addition of a to the correction coefficient k is performed continuously until C ≥ C1. Accordingly, the value of the correction coefficient k during this time continues to increase as shown in Fig. 9.

On the other hand, if it is judged at step 110 that $C \ge C_1$, the routine proceeds to step 112, where it is judged if the count C has become smaller than C_2 . When $C < C_2$, the processing cycle is ended. Therefore, as shown in Fig. 9, the correction coefficient k is held constant until $C \ge C_2$.

Next, at step 112, when it is judged that $C \ge C_2$, the routine proceeds to step 113, where β is subtracted from the correction coefficient k. Next,

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at step 113, it is judged if the correction coefficient k has become zero or a negative number. When k > 0, the processing cycle is ended. Accordingly, as shown in Fig. 9, the correction coefficient k is reduced until $k \le 0$. Note that, as mentioned later, if k > 0, the air-fuel mixture fed to the combustion chamber 3 is made rich and during this time the degree of richness is changed by the pattern shown in Fig. 9.

On the other hand, if it is judged at step 114 that $K \le 0$, the routine proceeds to step 115, where the NO_x release flag is rosot. Noxt, at step 116, ΣNO_x is made zoro. That is, at this timo, it is considered that all of the NO_x which had been absorbed in the NO_x absorbent 17 is released, so the estimated value ΣNO_x of the NO_x absorbed in the NO_x absorbent 17 is made zero. Next, at step 117, the count C and the correction coefficient k are made zero and the processing cycle is ended.

On the other hand, if it is judged at step 101 that $k \ge 1.0$, that is, when the engine operating state is one in which the air-fuel mixture should be made rich or the stoichiometric air-fuel ratio, the routine proceeds to step 118, where the count D is incremented by one. Next, at step 119, it is judged if the count D has become larger than the constant value D_0 . When $D > D_0$, the routine proceeds to step 120, where ΣNO_x is made zero. That is, when the combustion of the rich air-fuel ratio or the stoichiometric air-fuel ratio continues for a certain time, it may be considered that all of the NOx has been released from the NOx absorbent 17, so at this time the estimated value $\Sigma NO_{\boldsymbol{x}}$ of the amount of NO_x absorbed in the NO_x absorbent 17 is made zero.

Figure 14 shows the routine for calculation of the fuel injection time TAU. This routine is repeatedly executed.

Referring to Fig. 14, first, at step 150, a basic fuel injection time TP is calculated from a map indicated in Fig. 2. Subsequently, at step 151, the correction coefficient K shown in Fig. 3, which is determined in accordance with the operating state of the engine, is calculated. Next, at step 152, it is judged if the NOx release flag is set or not. When the NOx release flag is not set, the routine proceeds to step 153, where the correction coefficient K is made Kt. Next, at step 155, Kt is multiplied with the basic fuel injection time TP, whereby the fuel injection time TAU is calculated. Accordingly, at this time, the air-fuel mixture which is fed into the combustion chamber 3 is made lean, the stoichiometric air-fuel ratio, or rich in accordance with the operating state of the engine as shown in Fig. 3.

On the other hand, when it is judged at step 152 that the NO_{x} release flag is set, the routine proceeds to step 154, where K_{t} is made the sum (k

+ 1) of correction coefficient k calculated by the routine shown in Fig. 12 and Fig. 13 and 1, then the routine proceeds to step 155. Next, at this time, the air-fuel mixture fed to the combustion chamber 3 is made rich, then the degree of richness is changed by the pattern shown in Fig. 9.

Figure 15 shows another embodiment of the internal combustion engine. In this embodiment, an outlet side of a casing 18 is connected through an exhaust pipe 22 to a catalytic converter 24 housing a three-way catalyst 23. This three-way catalyst 23, as is well known, exhibits a high purification efficiency with respect to CO, HC, and NO_x when the air-fuel ratio is maintained near the stoichiometric air-fuel ratio, but the three-way catalyst 23 also has a high purification efficiency with respect to NO_x even when the air-fuel ratio becomes rich to a certain extent. In the embodiment shown in Fig. 15, a three-way catalyst 23 is provided downstream of the NO_x absorbent 17 so as to remove the NO_x using this characteristic.

That is, as is mentioned above, if the air-fuel mixture fed into the engine cylinder is made rich to release the NO_x from the NO_x absorbent 17, the NO_x absorbed in the NO_x absorbent 17 is rapidly released from the NO_x absorbent 17. At this time, the NO_x is reduced during its release, but there is a possibility that all of the NO_x will not be reduced. If the three-way catalyst 23 is disposed downstream of the NO_x absorbent 17, however, the NO_x which could not be reduced at the time of the release of the NO_x is reduced by the three-way catalyst 23. Accordingly, by disposing the three-way catalyst 23 downstream of the NO_x absorbent 17, it becomes possible to improve considerably the purification performance of the NO_x.

In the embodiments discussed up to here, use was made, as the NOx absorbent, of a NOx absorbent 17 comprised of at least one of an alkali metal, alkali earth, and rare earth and a precious metal carried on alumina. Instead of using such a NO_x absorbent 17, however, it is also possible to use a complex oxide of an alkali earth and copper, that is, a NO_x absorbent of the Ba-Cu-O system. As such a complex oxide of an alkali earth and copper, use may be made for example MnO₂ • BaCuO₂. In this case, it is also possible to add platinum Pt or cerium Ce. In a NO_x absorbent of the MnO2 • BaCuO2 system, the copper Cu performs the same catalytic function as the platinum Pt in the NO_x absorbent 17 spoken of up to now. When the air-fuel ratio is lean, the NO_x is oxidized by the copper (2NO + $O_2 \rightarrow 2NO_2$) and dispersed in the absorbent in the form of nitric acid ions

On the other hand, if the air-fuel ratio is rich, similarly, NO_x is released from the absorbent. This NO_x is reduced by the catalytic action of the cop-

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per Cu. The NO_x reducing ability of copper Cu, however, is weaker than the NO_x reducing ability of platinum Pt and therefore when using an absorbent of the Ba-Cu-O system, the amount of NO_x which is not reduced at the time of release of the NO_x becomes somewhat greater than with the NO_x absorbent 17 discussed up to now. Therefore, when using an absorbent of the Ba-Cu-O system, as shown in Fig. 21, it is preferable to dispose a three-way catalyst 23 downstream of the absorbent.

LIST OF REFERENCE NUMERALS

- 3 combustion chamber
- 5 intake valve
- 7 exhaust valve
- 16 exhaust pipe
- 17 NO_x absorbent
- 25 temperature sensor

Claims

- 1. An exhaust purification device of an internal combustion engine which has in an engine exhaust passage a NOx absorbent which absorbs the NO_x when the air-fuel ratio of the inflowing exhaust gas is lean and which releases the absorbed NOx when the air-fuel ratio of the inflowing exhaust gas becomes rich and which is provided with a temperature detecting means for detecting a temperature representing the temperature of the NO_x absorbent and a NOx release controlling means for making the air-fuel ratio of the exhaust gas flowing into the NOx absorbent rich when the NOx is to be released from the NOx absorbent and at that time increasing the degree of richness or shortening the time the ratio is made rich the higher the temperature representing the temperature of the NOx absorbent.
- 2. An exhaust purification device of an internal combustion engine according to claim 1, wherein said NO_x release controlling means increases the degree of richness and makes the time of making the ratio richer shorter the higher the temperature representing the temperature of the NO_x absorbent.
- 3. An exhaust purification device of an internal combustion engine according to claim 2, wherein said NO_x release controlling means changes the degree of richness by a pattern of change resembling the pattern of change of the amount of NO_x released from the NO_x absorbent when releasing NO_x from the NO_x absorbent.

- 4. An exhaust purification device of an internal combustion engine according to claim 3, wherein said NO_x release controlling means increases the degree of richness to a predetermined degree of richness by a predetermined rate of rise and then reduces the degree of richness by a predetermined rate of reduction when releasing NO_x from the NO_x absorbent and increases the rate of rise, the predetermined degree of richness, and the rate of reduction the higher the temperature representing the temperature of the NO_x absorbent.
- 5. An exhaust purification device of an internal combustion engine according to claim 1, wherein the temperature representing the NO_x absorbent is the temperature of the exhaust gas flowing into the NO_x absorbent.
- 6. An exhaust purification device of an internal combustion engine according to claim 5, wherein provision is made of a memory in which is previously stored the tempeature of the exhaust gas flowing into the NO_x absorbent as a function of the engine load and the engine rotational speed and wherein the temperature representing the temperature of the NO_x absorbent is stored in the memory.
- 7. An exhaust purification device of an internal combustion engine according to claim 1, wherein said NO_x release controlling means makes the air-fuel ratio of the air-fuel mixture fed into the combustion chamber rich when releasing NO_x from the NO_x absorbent.
 - 8. An exhaust purification device of an internal combustion engine according to claim 1, wherein NO_x estimating means is provided for estimating the amount of NO_x absorbed in said NO_x absorbent and wherein the NO_x release controlling means makes the air-fuel ratio of the exhaust gas flowing into the NO_x absorbent rich to release the NO_x from the NO_x absorbent when the amount of NO_x estimated to be absorbed in the NO_x absorbent by the NO_x estimating means exceeds a predetermined allowance.
- 9. An exhaust purification device of an internal combustion engine according to claim 8, wherein said NO_x estimating means estimates the amount of the NO_x absorbed in the NO_x absorbent on the basis of the amount of NO_x discharged from the combustion chamber to the engine exhaust passage.

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- 10. An exhaust purification device of an internal combustion engine according to claim 9, wherein said NO_x estimating means is comprised of a NO_x calculating means for calculating the amount of NO_x discharged per unit time from the engine to the engine exhaust passage in accordance with the engine load and the engine rotational speed and an cumulative adding means for cumulatively adding the amounts of NO_x calculated by the NO_x calculating means.
- 11. An exhaust purification device of an internal combustion engine according to claim 10, wherein said NO_x calculating means is provided with a memory in which is previously stored the amount of NO_x discharged per unit time from the engine to the engine exhaust passage as a function of the engine load and the engine rotational speed and wherein the cumulative adding means cumulatively adds the amounts of NO_x stored in the memory and determined from the engine load and the engine rotational speed.
- 12. An exhaust purification device of an internal combustion engine according to claim 10, wherein provision is made of a throttle valve disposed in the engine intake passage for controlling the engine load and the vacuum inside the engine intake passage downstream of the throttle valve is used as a value representing the engine load.
- 13. An exhaust purification device of an internal combustion engine according to claim 8, wherein said allowance is the maximum NO_x absorption capacity of the NO_x absorbent.
- 14. An exhaust purification device of an internal combustion engine according to claim 13, wherein said allowance is a function of the temperature representing the temperature of the NO_x absorbent.
- 15. An exhaust purification device of an internal combustion engine according to claim 8, wherein said NO_x estimating means makes the amount of NO_x estimated to be absorbed in the NO_x absorbent zero when the air-fuel ratio of the exhaust gas flowing into the NO_x absorbent is made rich due to the amount of NO_x estimated by the NO_x estimating means exceeding the allowance.
- 16. An exhaust purification device of an internal combustion engine according to claim 8, wherein air-fuel ratio control means is provided

- for making the air-fuel ratio of the air-fuel mixture fed to the combustion chamber rich in accordance with the operating state of the engine regardless of whether the amount of NO_x estimated by the NO_x estimating means exceeds the allowance.
- 17. An exhaust purification device of an internal combustion engine according to claim 16, wherein said air-fuel ratio control means makes the air-fuel ratio of the air-fuel mixture fed into the combustion chamber rich when the engine load is higher than a predetermined load.
- 18. An exhaust purification device of an internal combustion engine according to claim 17, wherein said NO_x estimating means makes the amount of NO_x estimated as being absorbed in the NO_x absorbent zero when the air-fuel ratio of the air-fuel mixture is made rich for more than a predetermined time.
- 19. An exhaust purification device of an internal combustion engine according to claim 1, wherein the NO_x absorbent includes at least one substance selected from alkali metals such as potassium, sodium, lithium, and cesium, alkali earths such as barium and calcium, and rare earths such as lanthanum and yttrium and platinum.
- 20. An exhaust purification device of an internal combustion engine according to claim 1, wherein the NO_x absorbent is comprised of a compound oxide of barium and copper.
- 21. An exhaust purification device of an internal combustion engine according to claim 1, wherein a three-way catalyst is disposed in the engine exhaust passage downstream of the NO_x absorbent.

Fig.1

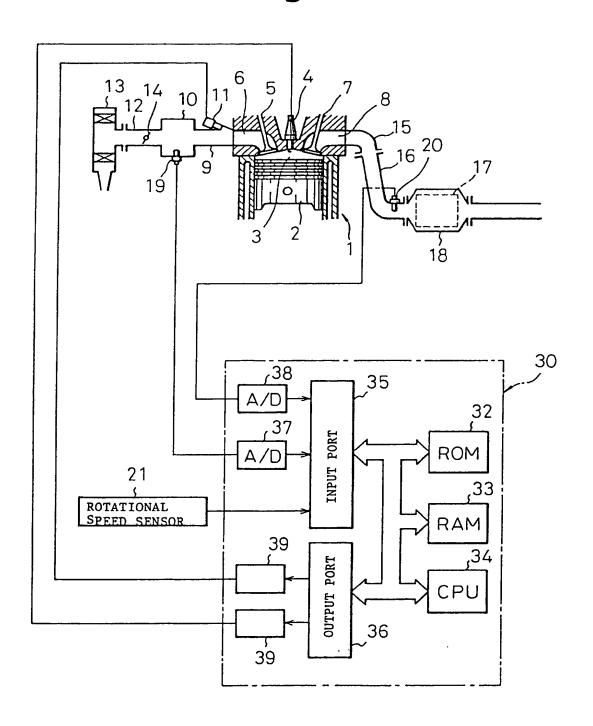


Fig.2

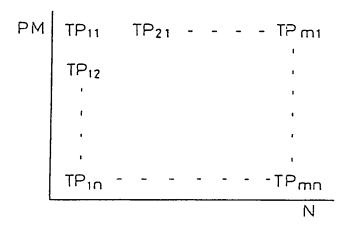


Fig.3

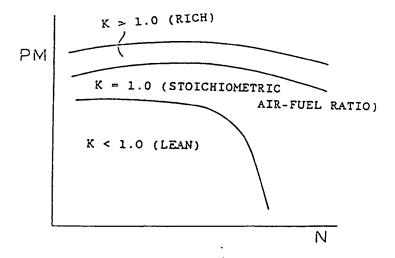


Fig.4

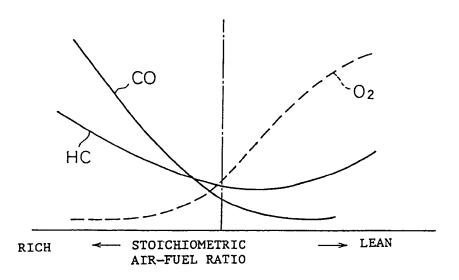
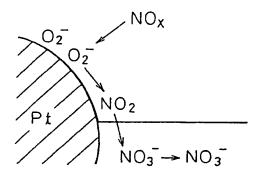


Fig.5(A)

Fig.5(B)



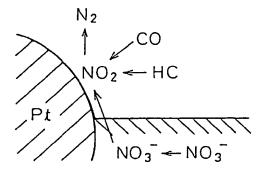


Fig.6(A)

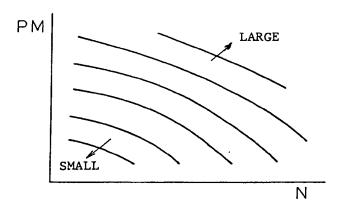


Fig.6(B)

РМ	N ₁₁	1	V 21	-		-	-	- Ni 1	
								•	
	N _{.12}							•	
	•							•	
	•							•	
	•							•	
	•							•	
	Nij	•	-	-	-	-	-	-Nij	
•								N	•

Fig.7

NO_X ABSORPTION CAPACITY

NO_X CAP

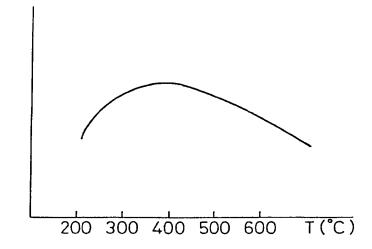


Fig.8

 $NO_{\mathbf{X}}$ CONCENTRATION

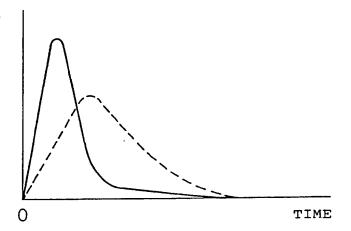
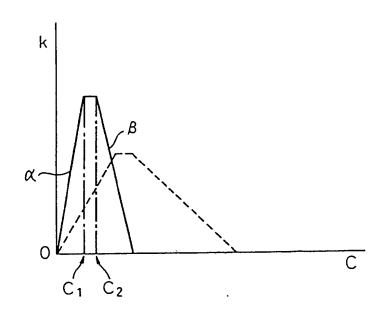


Fig.9



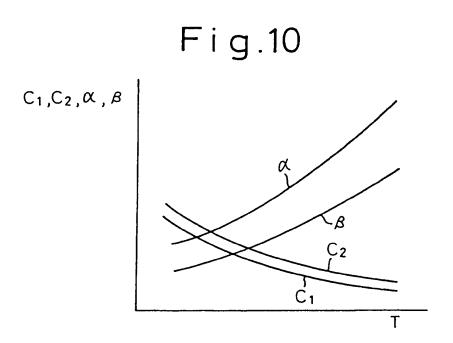


Fig.11

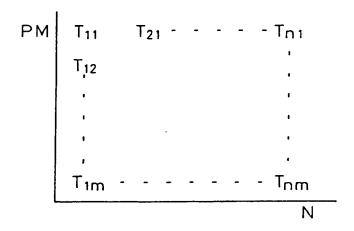


Fig. 12

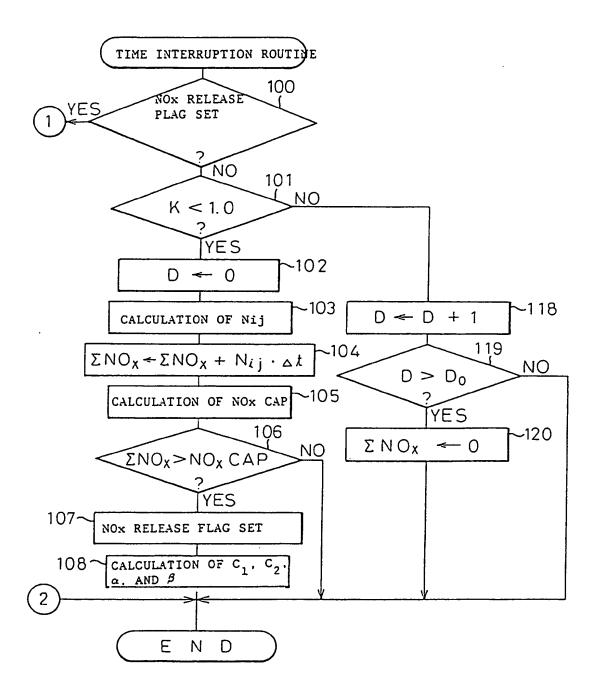


Fig.13

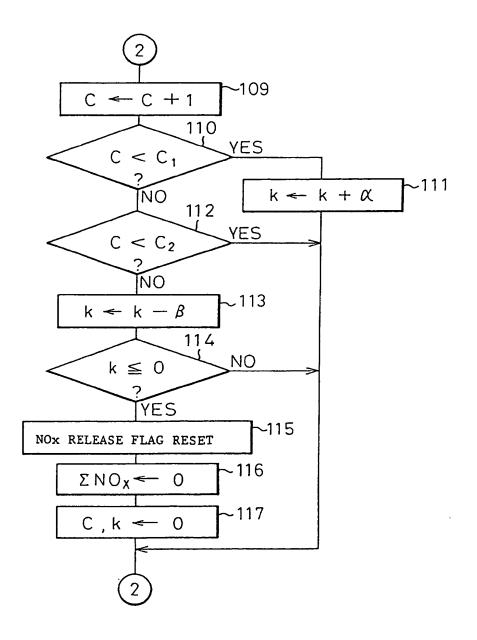


Fig.14

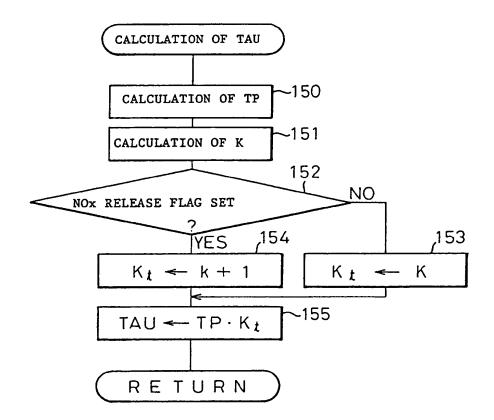
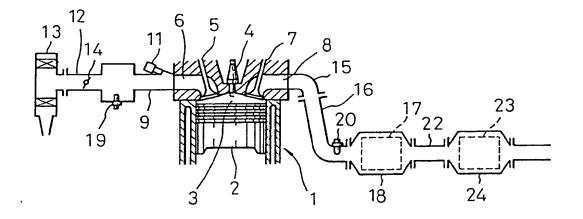


Fig.15



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP93/00777

	SSIFICATION OF SUBJECT MATTER						
		301D53/34, B01J23/58,	F02D41/02				
According to International Patent Classification (IPC) or to both national classification and IPC							
B. FIELDS SEARCHED							
Minimum documentation searched (classification system followed by classification symbols) Int. C1 ⁵ F01N3/28, F01N3/24, B01D53/34, B01J23/58, F02D41/02							
	·						
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuvo Shinan Koho 1926 - 1993							
Jitsuyo Shinan Koho 1926 - 1993 Kokai Jitsuyo Shinan Koho 1971 - 1993							
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)							
C. DOCUMENTS CONSIDERED TO BE RELEVANT							
Category*	Citation of document, with indication, where a	ppropriate, of the relevant passages	Relevant to claim No.				
A	JP, A, 2-149715 (Mazda Mot June 8, 1990 (08. 06. 90), Lines 3 to 13, column 3 (F	1-20					
A	JP, B2, 1-56816 (Ebara-Inf December 1, 1989 (01. 12. Lines 3 to 26, column 3 (F	1-20					
A	JP, A, 4-141219 (Mazda Mote May 14, 1992 (14. 05. 92), Line 13, column 4 to line (Family: none)	1-20					
A	JP, A, 3-194113 (Mazda Moto August 23, 1991 (23. 08. 9) Line 19, column 4 to line (Family: none)	1-20					
А	JP, U, 4-1617 (Toyota Motor January 8, 1992 (08. 01. 92 Lines 8 to 19, column 3 (Fa	1-20					
X Further documents are listed in the continuation of Box C. See patent family annex.							
Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "Beginning to general state of the art which is not considered to be of particular relevance "T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention							
"E" carlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other							
special n	eason (as specified) it referring to an oral disclosure, use, exhibition or other	"Y" document of particular relevance; the considered to involve an inventive : combined with one or more other such d	step when the document is				
P" document published prior to the international filing date but later than the priority date claimed "&" document member of the same patent family							
Date of the a	ctual completion of the international search	Date of mailing of the international sear	ch report				
July 2	8, 1993 (28. 07. 93)	August 17, 1993 (1	7. 08. 93)				
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Japan	ese Patent Office						
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP93/00777

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nation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Citation of document, with indication, where appropriate, of the rele	vant passages	Relevant to claim No
JP, A, 60-182325 (Toyota Motor Corp.), September 17, 1985 (17. 09. 85), Line 13, column 8 to line 7, column 9 & US, A, 4682577		12, 17
JP, A, 53-115687 (Matsushita Electric Ind. Co., Ltd.), October 9, 1978 (09. 10. 78), Line 4, column 1 to line 2, column 2 & JP, B2, 57-27739		19
JP, A, 64-30643 (Matsushita Electric Ind. Co., Ltd.), February 1, 1989 (01. 02. 89), Line 5, column 4 to line 10, column 5 (Family: none)		20
	Citation of document, with indication, where appropriate, of the relevance	Citation of document, with indication, where appropriate, of the relevant passages JP, A, 60-182325 (Toyota Motor Corp.), September 17, 1985 (17. 09. 85), Line 13, column 8 to line 7, column 9 & US, A, 4682577 JP, A, 53-115687 (Matsushita Electric Ind. Co., Ltd.), October 9, 1978 (09. 10. 78), Line 4, column 1 to line 2, column 2 & JP, B2, 57-27739 JP, A, 64-30643 (Matsushita Electric Ind. Co., Ltd.), February 1, 1989 (01. 02. 89), Line 5, column 4 to line 10, column 5

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